



# Mild oxidation of bulky organic compounds with hydrogen peroxide over mesoporous TiO<sub>2</sub>-SiO<sub>2</sub> xerogels prepared by non-hydrolytic sol-gel

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## ABSTRACT

The oxidation of bulky organic compounds with aqueous H<sub>2</sub>O<sub>2</sub> over a TiO<sub>2</sub>-SiO<sub>2</sub> xerogel catalyst prepared by a simple non-hydrolytic sol-gel route is described for the first time. Anthracene, cyclooctene, styrene, α-naphtol, diphenyl sulfide, dibenzothiophene and 4,6-dimethyl-dibenzothiophene were oxidized with high activity, selectivity and H<sub>2</sub>O<sub>2</sub> efficiency at moderate temperatures (40–60 °C). Moreover, a similar catalytic behavior was observed when *tert*-butyl hydroperoxide (TBHP) was used as an oxidizing agent. These excellent catalytic performances were ascribed to the unique texture of the catalyst (specific surface area 1200 m<sup>2</sup> g<sup>-1</sup>, pore volume 2.4 cm<sup>3</sup> g<sup>-1</sup>, average pore diameter 15 nm) and to the stability of Ti sites after exposure to aqueous H<sub>2</sub>O<sub>2</sub> or TBHP.

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## 1. Introduction

Liquid phase oxidation is widely used in the manufacturing of both fine and bulk chemicals. Many oxidation applications are traditionally carried out using organic peracids and inorganic compounds in stoichiometric amounts, which leads to the formation of numerous by-products and high volume of liquid waste. In order to overcome these problems, a number of catalytic methods using environmentally friendly oxidizing agents have been investigated. Transition-metal salts or complexes are commonly used as homogeneous catalysts for these processes, but significant research efforts have been directed to the development of heterogeneous catalysts for cleaner oxidation applications. Due to their excellent catalytic behavior, crystalline titanium-silicates, in the framework of which titanium (IV) is isomorphously substituted for silicon, are extensively used for both academic and industrial purposes [1–3].

Among the oxidants activated by these catalysts, hydrogen peroxide is particularly attractive for environmental and economical reasons [3,4].

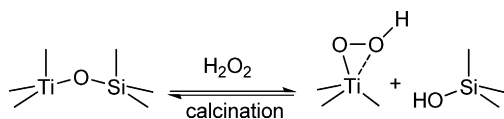
Since the discovery of titanium silicate-1 (TS-1) [5] and its capacity to catalyze mild oxidation with H<sub>2</sub>O<sub>2</sub> [6], a variety of crystalline and amorphous Ti-containing materials have been prepared. The crystalline titanium-silicates (TS-1, TS-2, Ti-beta, etc.) with zeolite framework are microporous. They are excellent catalysts for the oxidation of organic molecules with H<sub>2</sub>O<sub>2</sub>, but they are limited to small substrates because of their small pore size.

As a result, much work has been dedicated to the synthesis of mesoporous amorphous TiO<sub>2</sub>-SiO<sub>2</sub> mixed oxides. The grafting of hydrolyzable Ti compounds to silica carriers is the simplest route. Ti-containing mesoporous templated silica (Ti-MCM-41, Ti-MCM-48) with uniform mesopores promised to open new opportunities for the oxidation of bulky molecules [7–9]. TiO<sub>2</sub>-SiO<sub>2</sub> mixed oxides have been prepared by conventional sol-gel processes based on the hydrolysis and condensation of silicon and titanium alkoxides. However, the xerogels obtained by vacuum-drying were usually microporous [10,11] and elaborate drying procedures (such as extraction with supercritical CO<sub>2</sub> or silylation of the gels before drying) were needed to obtain mesoporous materials [12].

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**Scheme 1.** Formation of the Ti-peroxo sites.

Unfortunately, the amorphous  $\text{TiO}_2$ - $\text{SiO}_2$  materials usually exhibited much lower catalytic performance (in terms of activity and  $\text{H}_2\text{O}_2$  efficiency) than the crystalline titanosilicates in the oxidation of organic substrates with aqueous solutions of  $\text{H}_2\text{O}_2$  and thus their use was limited to oxidation reactions with dry organic hydroperoxides. This behavior has been ascribed to the much higher hydrophilicity of the amorphous materials leading to extensive water adsorption hindering the access to the Ti(IV) active sites [3,13] and also to the irreversible deactivation of these sites in the presence of aqueous  $\text{H}_2\text{O}_2$  [14–17].

Indeed, the superior catalytic properties of TS-1 can be related to its structural stability: the cleavage of the Si–O–Ti bonds by  $\text{H}_2\text{O}_2$  (involved in the formation of the active peroxo sites from  $\text{Ti}(\text{OSi})_4$  sites) was reversible upon calcination (Scheme 1) [14–16]. By contrast, in the case of amorphous Ti(IV)-grafted silica materials (Ti-MCM-41 and Ti- $\text{SiO}_2$  Aerosil), the exposure to aqueous  $\text{H}_2\text{O}_2$  led to the irreversible cleavage of Si–O–Ti bonds and to the formation of extraframework  $\text{TiO}_2$  during the subsequent calcination, while the cleavage of Si–O–Ti bonds was reversible after exposure to dry *tert*-butyl hydroperoxide (TBHP) in decane and calcination [17]. These amorphous materials were poor catalysts for the olefin epoxidation with  $\text{H}_2\text{O}_2$  but they showed good activity in the epoxidation with TBHP.

An original sol–gel process based on non-hydrolytic condensations between chloride and alkoxide groups is being developed in University of Montpellier [18]. This process offers a very simple and efficient route to obtain homogeneous  $\text{TiO}_2$ - $\text{SiO}_2$  xerogels starting from cheap precursors, without any organic templating agent. Furthermore, owing to the high degree of condensation of non-hydrolytic gels, mesoporous xerogels with high surface area and pore volumes can be obtained by simple evaporative drying, thus avoiding a supercritical drying step [19].

Although there are still very few examples of catalysts prepared by non-hydrolytic sol–gel, this process appears particularly promising for the one-step synthesis of mixed oxide catalysts, such as Nb–V(–M) oxides (M = Mo, Sb, Si) for the oxidative dehydrogenation of propane [20],  $\text{TiO}_2$ - $\text{V}_2\text{O}_5$  catalysts for the SCR of  $\text{NO}_x$  by  $\text{NH}_3$  [21] or the total oxidation of volatile organic compounds [22],  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ - $\text{MoO}_3$  catalysts for alkene metathesis [23] and  $\text{TiO}_2$ - $\text{SiO}_2$ (– $\text{MeSiO}_{1.5}$ )(– $\text{Me}_3\text{SiO}_{0.5}$ ) for the epoxidation of alkenes with organic hydroperoxides [24,25].

The non-hydrolytic sol–gel method offers a very simple and efficient route to mesoporous  $\text{TiO}_2$ - $\text{SiO}_2$  xerogels with a high dispersion of Ti species, avoiding the use of templates or supercritical drying. Recently we found that these materials exhibited excellent performance in the mild oxidation of sulfides, sulfoxides and thiophenes with aqueous solutions of  $\text{H}_2\text{O}_2$  [26,27]. This behavior has been related to the high degree of condensation, typical of non-hydrolytic  $\text{TiO}_2$ - $\text{SiO}_2$  xerogels, which resulted in a low density of surface silanols and low hydrophilicity.

In the present study we report for the first time about the successful use of a non-hydrolytic  $\text{TiO}_2$ - $\text{SiO}_2$  xerogel as catalyst for the oxidation of organic substrates less reactive than the sulfided ones such as bulky olefins, aromatics and phenols with aqueous solutions of  $\text{H}_2\text{O}_2$ . The effect of different parameters on the catalytic behavior was particularly studied in the case of styrene. Also, the nature and the stability of the Ti species generated during the interaction of this  $\text{TiO}_2$ - $\text{SiO}_2$  xerogel with  $\text{H}_2\text{O}_2$  or TBHP was inves-

tigated using diffuse reflectance UV–vis spectroscopy (DR UV–vis). TS-1 was used as a reference for some oxidation tests.

## 2. Experimental part

### 2.1. Synthesis and characterization of the $\text{TiO}_2$ - $\text{SiO}_2$ catalyst

A  $\text{TiO}_2$ - $\text{SiO}_2$  gel mixed oxide with a nominal Ti content of 4.6 wt% was prepared by the reaction of  $\text{SiCl}_4$  and  $\text{TiCl}_4$  with  $^i\text{Pr}_2\text{O}$ . In a glovebox under argon atmosphere,  $\text{SiCl}_4$  (6.6 g, 38.8 mmol),  $\text{TiCl}_4$  (0.46 g, 2.4 mmol),  $^i\text{Pr}_2\text{O}$  (8.17 g, 80 mmol) and  $\text{CH}_2\text{Cl}_2$  (10 mL) were added successively with a syringe into a 150-mL, Teflon-lined stainless steel autoclave. The autoclave was heated under autogenous pressure for 6 days at  $150^\circ\text{C}$ . After cooling, the autoclave was opened in a glovebox. The gel was filtered off, washed three times with dry  $\text{CH}_2\text{Cl}_2$ , dried under vacuum first at room temperature for 2 h, then at  $110^\circ\text{C}$  for 6 h, and calcined in dry air at  $500^\circ\text{C}$  for 5 h. The mixed oxides were stored in a dry atmosphere prior to be characterized or used as oxidation catalysts.

TS-1 with a nominal Ti content of 1.2 wt% was prepared by direct hydrothermal synthesis according to the method reported in Ref. [27].

The Ti content of materials was determined by ICP-MS at the “Service Central d’Analyse” USR-59/CNRS.  $\text{N}_2$  physisorption experiments were carried out at  $-196^\circ\text{C}$  on a Micromeritics ASAP 2010 sorptometer; the sample was previously degassed under vacuum at  $200^\circ\text{C}$  for 15 h. The pore size distribution was obtained from the desorption branch using the BJH method and the Harkins–Jura standard isotherm. Diffuse reflectance UV–vis (DR UV–vis) spectra were recorded under ambient conditions on a PerkinElmer Lambda 14 spectrometer equipped with a  $\text{BaSO}_4$  coated integration sphere; the samples were diluted in  $\text{BaSO}_4$ ; the spectra were plotted using the Kubelka–Munk function.

### 2.2. Procedure for oxidation reaction

The catalytic oxidation reactions were performed at atmospheric pressure in a thermostated glass batch reactor, equipped with magnetic stirrer, thermometer, and condenser. In a typical experiment, 50 mg of catalyst was suspended under stirring (800 rpm) in a mixture containing the organic substrate dissolved in 15 mL of solvent. The adequate volume of hydrogen peroxide (50 wt% aqueous solution) was added at the beginning of experiment. Blank runs were carried out by mixing the reactants in the absence of catalyst. Samples of the reaction mixture were withdrawn periodically and analyzed on a Varian 3900 chromatograph equipped with a capillary column (DB-1, 60 m, 0.20 mm i.d., 0.25  $\mu\text{m}$  film thickness). The hydrogen peroxide concentration was measured by iodometric titration.

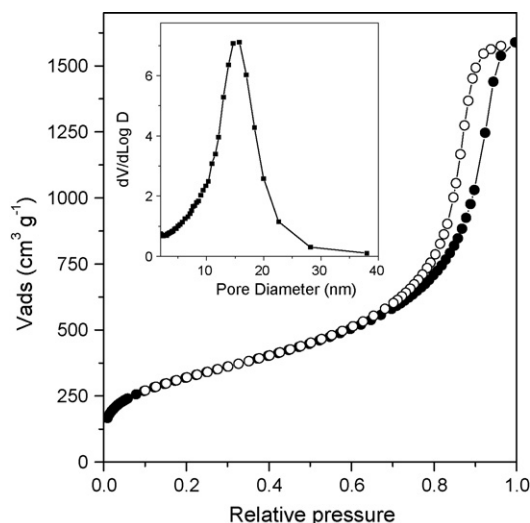
## 3. Results and discussion

### 3.1. Synthesis and characterization of $\text{TiO}_2$ - $\text{SiO}_2$ xerogel

The  $\text{TiO}_2$ - $\text{SiO}_2$  catalyst used in this study (denoted as NH  $\text{TiO}_2$ - $\text{SiO}_2$ , NH for non-hydrolytic) was prepared in one-step by thermal reaction of  $\text{SiCl}_4$  and  $\text{TiCl}_4$  with di-isopropyl ether ( $^i\text{Pr}_2\text{O}$ ) in  $\text{CH}_2\text{Cl}_2$  under autogeneous pressure. The formation of the oxide network results from the etherolysis and condensation of the chloride precursors (Eqs. (a) and (b)) (M = Si or Ti):



The condensation reactions around Si atoms are promoted by Ti species. The texture of the resulting  $\text{TiO}_2$ - $\text{SiO}_2$  xerogels can be con-



**Fig. 1.**  $N_2$  adsorption-desorption isotherm at  $-196^\circ\text{C}$  and pore size distribution (inset) of  $\text{NH TiO}_2\text{-SiO}_2$ .

trolled by the synthesis parameters (temperature, reaction time, liquid phase volume, Ti content) [19]. Optimization of the different parameters allowed us to synthesize at  $150^\circ\text{C}$  a catalyst with a  $\text{Ti}/(\text{Si} + \text{Ti})$  molar ratio of 0.06 and a remarkable mesoporous texture. The textural properties derived from the nitrogen physisorption isotherm (Fig. 1) are outstanding, with a specific surface area of  $1170\text{ m}^2\text{ g}^{-1}$  and a pore volume of  $2.4\text{ cm}^3\text{ g}^{-1}$ . The pore size distribution derived from a BJH analysis of the desorption isotherm showed a monomodal distribution centered at about 15 nm. t-Plot analysis showed that the volume of micropores was negligible ( $<0.02\text{ cm}^3\text{ g}^{-1}$ ).

TS-1 ( $\text{Ti}/(\text{Si} + \text{Ti})$  molar ratio of 0.015) displayed an isotherm of type I (not shown), which revealed its microporous nature. The specific surface area and pore volume were  $400\text{ m}^2\text{ g}^{-1}$  and  $0.1\text{ cm}^3\text{ g}^{-1}$ , respectively.

The distribution of the Ti atoms in the silica framework was investigated using DR UV-vis spectroscopy. The DR UV-vis spectrum of the calcined  $\text{TiO}_2\text{-SiO}_2$  xerogel (see below, Fig. 2, spectrum a) exhibited two main absorption bands centred at about 210 and

260 nm. The band at 210 nm is attributed to the isolated Ti atoms in a tetrahedral coordination environment [28–32], whereas the band centred at 260 nm indicated the presence of higher-coordinated Ti atoms in oligomeric Ti species or possibly of very small  $\text{TiO}_2$  nano-domains (quantum size effect) [33–35]. The absence of a band at 330 nm showed that anatase was not present in significant quantities. TS-1 showed only a well-defined band at 210 nm.

### 3.2. Oxidation of bulky organic molecules over $\text{NH TiO}_2\text{-SiO}_2$

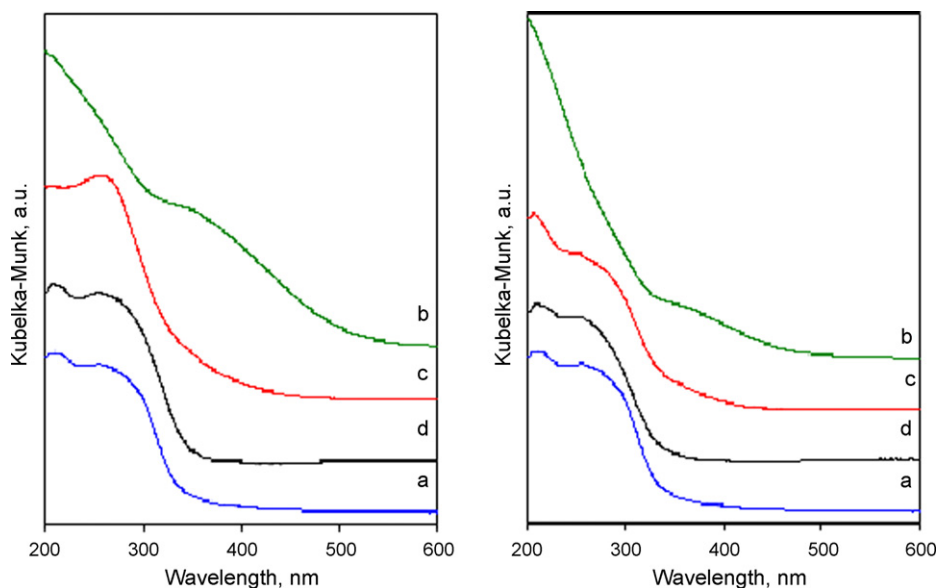
To evaluate the potential of the non-hydrolytic  $\text{TiO}_2\text{-SiO}_2$  mixed oxide catalyst in the oxidation with  $\text{H}_2\text{O}_2$ , anthracene, cyclooctene, styrene,  $\alpha$ -naphthol, diphenyl sulfide, dibenzothiophene (DBT) and 4,6-dimethyl-dibenzothiophene (4,6-DMDBT) were chosen as representative molecules for different classes of organic compounds. The main oxidation product(s) (representing more than 95% of product mixture) are displayed in Scheme 2 for each reaction.

9,10-Anthraquinone, obtained by oxidation of anthracene (reaction 1), is an important intermediate for the manufacturing of pigments, dyes and  $\text{H}_2\text{O}_2$ . Industrially, the anthracene oxidation is performed either in the liquid phase with  $\text{CrO}_3$  ( $50\text{--}105^\circ\text{C}$ ) or in the gas phase with air ( $340\text{--}390^\circ\text{C}$ ) over iron vanadate catalysts [36]. Two homogeneous catalytic systems have been recently proposed for anthracene conversion into anthraquinone with  $\text{H}_2\text{O}_2$  [37,38], but no heterogeneous catalyst was reported for this reaction.

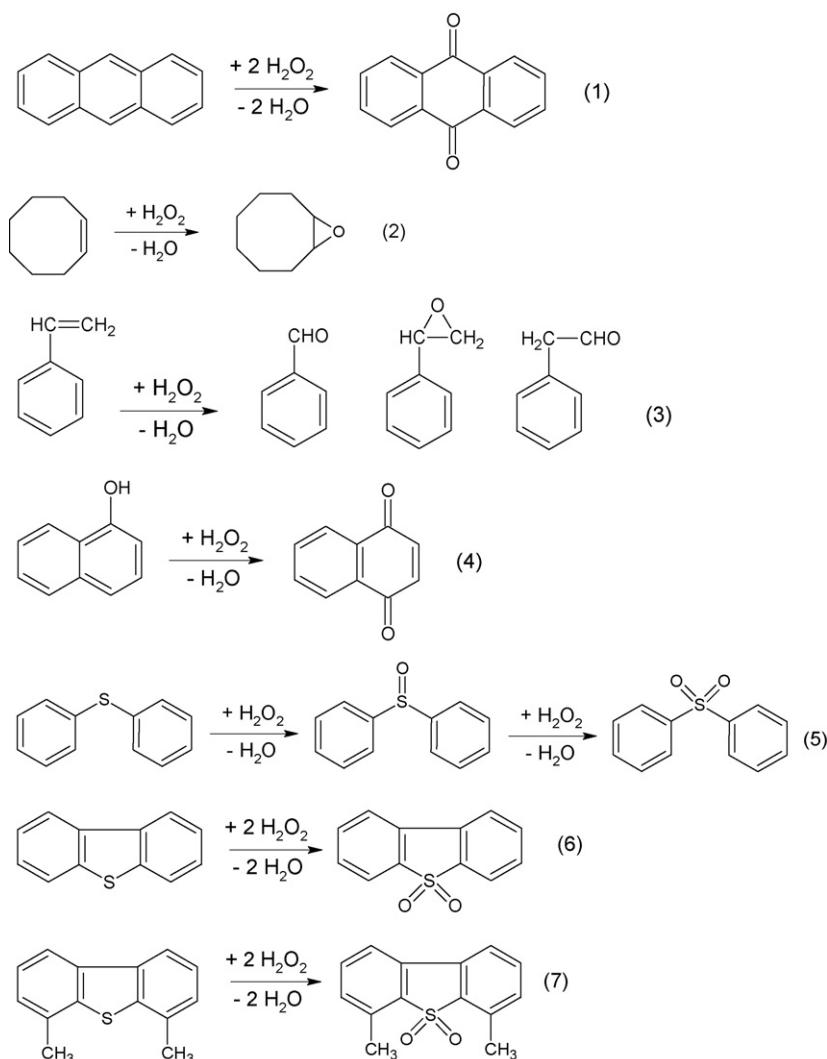
Cyclooctene oxidation (reaction 2) was chosen as a model reaction for the preparation of epoxides, which are versatile intermediates for fine and bulk chemicals production. This reaction has often been used in the evaluation of various mesoporous catalytic materials [39–45].

The oxidation of styrene by hydrogen peroxide (reaction 3) is of considerable interest for the synthesis of styrene oxide (SO), benzaldehyde (BzA) and phenylacetaldehyde (PhAA). As previously reported [46,47], the products distribution strongly depends on the catalyst topology and reaction conditions.

The oxidation of  $\alpha$ -naphthol, a monohydroxy aromatic compound (reaction 4), is a model reaction for the preparation of quinones. Usually this reaction is performed with potentially hazardous stoichiometric oxidizing agents, such as chromates, chlorides, mineral acids, peracids, etc. Consequently, catalytic methods using cleaner oxidizing agents are needed.



**Fig. 2.** DR UV-vis spectra of  $\text{NH TiO}_2\text{-SiO}_2$ : calcined (curve a); after adsorption of  $\text{H}_2\text{O}_2$  (left, curve b) or TBHP (right, curve b) then followed by thermal activation in air at  $80^\circ\text{C}$  (curve c) and  $550^\circ\text{C}$  (curve d).



**Scheme 2.** Oxidation reactions catalyzed by  $\text{NH TiO}_2\text{-SiO}_2$  and major reaction products obtained.

The oxidation of sulfides and thiophene derivatives (reactions 5–7) can be considered as model reactions for two important industrial applications: (i) sulfoxides and sulfones synthesis and (ii) sulfur removal from fuels (catalytic oxidative desulfurization) [48–50].

The catalytic reactions were carried out in an organic solvent (acetonitrile or methanol) fully miscible with the organic substrate and the hydrogen peroxide solution. In the absence of catalyst, using the same experimental conditions, the oxidation reaction occurred with insignificant substrate conversion (<2%). We compared the catalytic results obtained in the DBT oxidation with  $\text{H}_2\text{O}_2$  carried out in the presence of air to those obtained under nitrogen inert atmosphere. The differences between the catalytic behaviors were insignificant. In addition, no substrate conversion was observed in the experiments performed with the catalyst but in the absence of  $\text{H}_2\text{O}_2$ , indicating that under these mild conditions the oxygen from air was not activated by the catalyst.

The reaction conditions and the catalytic behavior obtained for each organic molecule are summarized in Table 1.

For all the organic substrates, the oxidation reactions occurred with significant conversions. With the exception of styrene, the conversions were higher than 65% after 360 min at 60 °C.

These data indicate, on the one hand, the high intrinsic activity of the Ti sites with  $\text{H}_2\text{O}_2$ , and on the other hand, the very beneficial

effect of the catalyst mesoporosity for the accessibility and mobility of large molecules inside pores.

In all catalytic tests,  $\text{H}_2\text{O}_2$  was mainly consumed in the oxidation reaction, but the direct decomposition of the oxidizing agent into water and oxygen was also observed. As expected, the  $\text{H}_2\text{O}_2$  efficiency (selectivity) depended on the temperature and substrate reactivity (implicitly of the reaction time). Selectivities in oxidized products higher than 90% were obtained in the most of catalytic tests.

Under the present conditions, the oxidation of phenyl sulfide and thiophenes over  $\text{NH TiO}_2\text{-SiO}_2$  was highly selective to the sulfur atom. Thus, phenyl sulfide was converted into sulfoxide and sulfone, whereas the oxidation of DBT and 4,6-DMDBT led directly to the corresponding sulfone. It is important to point out that 4,6-DMDBT, a poorly reactive molecule which is present in the fuels processed by the hydrosulfurization plants, can be effectively oxidized with  $\text{H}_2\text{O}_2$  in diluted methanol solution. Methanol was used as the solvent in this test because 4,6-DMDBT is not soluble in acetonitrile.

The catalytic oxidation of styrene and DBT was also carried out in the presence of anhydrous TBHP as an oxidant. The results included in Table 1 indicate that under similar conditions the catalytic behaviors of  $\text{H}_2\text{O}_2$  and TBHP were very close. As known [3,12,13], the dry TBHP is currently used as oxidant in the pres-

**Table 1**Reaction conditions, substrate conversion, H<sub>2</sub>O<sub>2</sub> efficiency and selectivity for the oxidation of different molecules catalyzed by NH TiO<sub>2</sub>-SiO<sub>2</sub>.

Substrate (S)	OA <sup>b</sup>	OA/S (mol/mol)	C <sub>i</sub> <sup>c</sup> (mol/L)	T (°C)	Time(min)	Conv. (%)	H <sub>2</sub> O <sub>2</sub> eff. <sup>d</sup> (%)	Products <sup>f</sup> (%)
Anthracene	H <sub>2</sub> O <sub>2</sub>	5/1	0.01	60	360	92	91	AQ (>95)
Cyclooctene	H <sub>2</sub> O <sub>2</sub>	5/1	0.08	60	360	67	90	COO (>95)
Styrene	H <sub>2</sub> O <sub>2</sub>	5/1	0.1	60	360	48	85	SO (9) BzA (78) PhAA (11)
	"	"	"	"	1000	77	80	SO (11) BzA (78) PhAA (6)
Styrene	TBHP	5/1	0.1	60	360	52	N.A. <sup>e</sup>	SO (3) BzA(88) PhAA (2)
α-Naphthol	H <sub>2</sub> O <sub>2</sub>	5/1	0.01	60	360	65	87	NQ (>95)
Phenylsulfide	H <sub>2</sub> O <sub>2</sub>	2/1	0.06	40	120	100	99	PSO (15) PS (85)
DBT	H <sub>2</sub> O <sub>2</sub>	2/1	0.1	60	120	97	98	DBTS (>99)
DBT	TBHP	2/1	0.1	60	120	97	N.A.	DBTS (>99)
4,6-DMDBT <sup>a</sup>	H <sub>2</sub> O <sub>2</sub>	2/1	0.01	60	120	60	N.A.	DMDBTS (>99)
	"	"	"	"	240	80	90	DMDBTS (>99)

Conditions: solvent = acetonitrile, 50 mg catalyst for 15 mL solution.

<sup>a</sup> Solvent = methanol.<sup>b</sup> Oxidizing agent.<sup>c</sup> Initial concentration of substrate.<sup>d</sup> H<sub>2</sub>O<sub>2</sub> efficiency = (mole of H<sub>2</sub>O<sub>2</sub> consumed in the oxidation)/(mole H<sub>2</sub>O<sub>2</sub> converted) × 100.<sup>e</sup> N.A.: non analyzed.<sup>f</sup> AQ: 9,10-anthraquinone; COO: cyclooctene oxide; SO: styrene oxide; BzA: benzaldehyde; PhAA: phenylacetaldehyde; NQ: 1,4-naphthoquinone; PSO: phenyl sulfoxide; PS: phenyl sulfone; DBTS: dibenzothiophene sulfone; DMDBTS: 4,6-dimethyl-dibenzothiophene sulfone.

ence of amorphous mesoporous materials (Ti-MCM-41, TiO<sub>2</sub>-SiO<sub>2</sub>), because the activity of these catalysts with hydrogen peroxide is very low.

In order to emphasize the favourable effect of the porosity, the catalytic behavior of NH TiO<sub>2</sub>-SiO<sub>2</sub> was compared with that of the microporous TS-1 titanosilicate. Table 2 shows the initial rate, the conversion and the TOF for two model substrates (MPS and DBT) oxidized under similar conditions. In the case of the oxidation of MPS, which can penetrate the pores of both catalysts, the activity of TS-1 (expressed in terms of TOF = mole of substrate converted/mole of Ti × hour) is higher than the activity of NH TiO<sub>2</sub>-SiO<sub>2</sub>. As expected, the intrinsic activity of the Ti atoms in TS-1 is remarkable. On the contrary, when a larger molecule such as DBT was oxidized, NH TiO<sub>2</sub>-SiO<sub>2</sub> proved significantly more active than TS-1. This result indicates clearly that DBT easily penetrates the large mesopores of NH TiO<sub>2</sub>-SiO<sub>2</sub> (15 nm), contrary to the TS-1 micropores (three-dimensional channel system with 0.53 nm × 0.56 nm aperture).

To obtain information on the stability of active Ti species in the NH TiO<sub>2</sub>-SiO<sub>2</sub> matrix, the catalyst was reused 4 times in the DBT oxidation reaction at 60 °C for 60 min in acetonitrile with a ratio H<sub>2</sub>O<sub>2</sub>/DBT of 2. The catalyst was separated by filtration after each reaction, washed with acetonitrile, and then placed into a fresh reagent mixture. The conversion of DBT was higher than 95% for all the catalytic cycles, indicating that the catalyst was stable under these conditions. Moreover, no changes in product selectivity and H<sub>2</sub>O<sub>2</sub> efficiency were observed during the different runs. On the other hand, to demonstrate that the activity of our catalyst was not due to the leaching of Ti species, an additional catalytic test was performed with DBT: the catalyst was filtered off at 60 °C after 15 min reaction (35% conversion) then the solution was further reacted for 60 min at 60 °C. Only a small increase in conversion of DBT (from 35 to 37%) was observed.

### 3.3. Styrene oxidation with H<sub>2</sub>O<sub>2</sub> over NH TiO<sub>2</sub>-SiO<sub>2</sub>

In order to obtain information on the effect of several parameters on the NH TiO<sub>2</sub>-SiO<sub>2</sub> catalytic activity and selectivity, oxidation tests using styrene and H<sub>2</sub>O<sub>2</sub> were carried out. The oxidation of styrene with H<sub>2</sub>O<sub>2</sub> has been largely studied over the last decade because of its importance in the production of aromatic intermediates [51–59]. A variety of Ti-containing catalysts, including microporous crystalline materials [51–54] and amorphous mesoporous materials [55–59] were tested in this reaction. Generally, moderate styrene conversions and styrene oxide selectivities were obtained. It was found that the product distribution is affected by several factors including catalyst topology and reaction conditions. Thus, a high selectivity to PhAA can be obtained with TS-1 [47,52,60], whereas the BzA formation is predominant on Ti-beta [47], mesoporous Ti-silicates, like Ti-MCM-41 [61], Ti-SBA-15 [55,57,62], Ti-SBA-1 [52–54] and mesoporous titanium–phosphorus mixed oxides [62]. A considerable increase in the styrene oxide selectivity was obtained over TS-1 in the presence of sodium hydroxide [63] or using anhydrous urea–H<sub>2</sub>O<sub>2</sub> adduct as oxidizing agent [10]. Also, it should be noted that the products' distribution in the olefin epoxidation strongly depended on the method of H<sub>2</sub>O<sub>2</sub> addition to the reaction system [64,65].

Playing on different reaction parameters (temperature, mode of addition of H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>/styrene ratio, solvent) led to very different catalytic behaviors (Table 3). Thus, when the temperature (entries 1–3) or the H<sub>2</sub>O<sub>2</sub>/styrene ratio (entries 6, 2, 5) was increased, the initial rate and styrene conversion significantly increased. The catalytic activity also depended on the nature of the solvent (entry 2 vs. entry 4): under similar conditions, a higher activity was obtained with acetonitrile than with methanol. In addition, when the oxidation of styrene was carried out in methanol (entry 4), the glycol monoether (1-methoxy-1-phenyl-ethan-2-ol) was a major prod-

**Table 2**Oxidation of methyl-phenyl sulfide (MPS) and dibenzothiophene (DBT) over TS-1 and NH TiO<sub>2</sub>-SiO<sub>2</sub> catalysts.

Catalyst	Substrate	Initial rate (M h <sup>-1</sup> g <sub>cat</sub> <sup>-1</sup> )	Reaction time (min)	Conversion (%)	TOF <sup>a</sup> (h <sup>-1</sup> )
TS-1	MPS	3.97	15	59	144
NH TiO <sub>2</sub> -SiO <sub>2</sub>	MPS	6.74	15	98	61
TS-1	DBT	0.12	30	3	3.2
NH TiO <sub>2</sub> -SiO <sub>2</sub>	DBT	2.68	30	67	21

Conditions: solvent = acetonitrile; H<sub>2</sub>O<sub>2</sub>/Substrate = 2/1; C<sub>0</sub> = 0.1 M; C<sub>cat</sub> = 3.33 g L<sup>-1</sup>.<sup>a</sup> TOF = mole of substrate converted/mole of Ti × hour.



**Table 3**Catalytic performances in styrene oxidation with H<sub>2</sub>O<sub>2</sub> over TiO<sub>2</sub>-SiO<sub>2</sub> xerogel.

Entry	T (°C)	Initial ratio H <sub>2</sub> O <sub>2</sub> /Styrene (mol/mol)	Initial rate (mol L <sup>-1</sup> h <sup>-1</sup> g <sub>catal</sub> <sup>-1</sup> )	Styrene conv. (%)	Product selectivity (%mol)				H <sub>2</sub> O <sub>2</sub> eff. (%)
					SO	BzA	PhAA	Other <sup>c</sup>	
1	40	5/1	0.17	21	8	90	2	Trace	93
2	60	5/1	0.54	48	9	78	11	2	85
3	80	5/1	1.10	55	8	75	11	6	71
4	60 <sup>a</sup>	5/1	0.32	39	2	55	7	36 <sup>d</sup>	87
5	60	7.5/1	0.65	67	8	75	10	7	80
6	60	1/1	0.13	18	9	74	17	Trace	90
7	60	1/1 <sup>b</sup>	–	21	49	34	13	4	95

Conditions: reaction time = 360 min, solvent = acetonitrile.

SO: styrene oxide; BzA: benzaldehyde; PhAA: phenylacetaldehyde.

<sup>a</sup> Solvent = methanol.<sup>b</sup> H<sub>2</sub>O<sub>2</sub> was added dropwise over 120 min.<sup>c</sup> 1-Phenyl-1,2-ethanediol; benzoic acid.<sup>d</sup> 1-methoxy-1-phenyl-2-ethanol.

uct (36% selectivity), due to the fact that the methanol is easily involved into the alcoholytic splitting reaction of the primary oxidation products [47]. When the H<sub>2</sub>O<sub>2</sub> was added in one shot to the acetonitrile/styrene mixture (entries 1–3,5,6), the major product was benzaldehyde (BzA) (>74%). The selectivity towards SO was less than 10% and the selectivity to PhAA varied from 2 to 17%. By-products, such as 1-phenyl-ethan-1,2-diol and benzoic acid, were obtained in low amounts. The selectivity for SO and BzA remains unchanged in spite of large variation in the H<sub>2</sub>O<sub>2</sub>/styrene ratio.

It is interesting to observe that the selectivity towards SO strongly increased (up to 49%) when H<sub>2</sub>O<sub>2</sub> was added dropwise over 2 h (entry 7 vs. entry 6). This is in line with the results recently reported by Guidotti et al. [65] showing that a minimal local H<sub>2</sub>O<sub>2</sub> concentration in the surroundings of Ti sites (obtained by slow addition of H<sub>2</sub>O<sub>2</sub>) is crucial for a highly selective olefin epoxidation.

Generally, good selectivity towards H<sub>2</sub>O<sub>2</sub> consumption was achieved for all the catalytic tests (Table 3). However, this selectivity depended on the oxidation conditions. For instance, it decreased from 93 to 71% when the temperature increased from 40 to 80 °C. Also, as the H<sub>2</sub>O<sub>2</sub>/Styrene ratio increased from 1/1 to 7.5/1, the H<sub>2</sub>O<sub>2</sub> efficiency decreased from 90 to 80%.

### 3.4. DR UV–vis spectroscopy

As discussed in Section 1, the Ti sites of TS-1 can be regenerated after exposure to aqueous H<sub>2</sub>O<sub>2</sub> (Scheme 1) without loss in activity, whereas amorphous Ti-SiO<sub>2</sub> aerosil or Ti-MCM-41 was irreversibly deactivated. DR UV–vis spectroscopy is the most commonly used technique in these investigations. Using this technique, we investigated the nature of the Ti species resulting from the interaction of NH TiO<sub>2</sub>-SiO<sub>2</sub> with H<sub>2</sub>O<sub>2</sub> and TBHP following the procedure reported by Gianotti et al. [17]. The DR UV–vis spectra of NH TiO<sub>2</sub>-SiO<sub>2</sub>/oxidant system under different treatment conditions are plotted in Fig. 2. The spectrum of untreated NH SiO<sub>2</sub>-TiO<sub>2</sub> (spectrum a) exhibited two main absorption bands at 210 and 260 nm assigned to Ti isolated sites and oligomeric Ti species, respectively (see Section 3.1).

The treatment of NH TiO<sub>2</sub>-SiO<sub>2</sub> with H<sub>2</sub>O<sub>2</sub> or TBHP produced a rapid change of the catalyst color from white to pale yellow and UV spectra showed the apparition of an additional broad band at about 370 nm (Fig. 2, spectra b). In the literature [15,66–71], this band is usually attributed to bidentate (η<sup>2</sup>) titanium hydroperoxo species. After drying for 1 h at 80 °C, the band at 370 nm drastically diminished (spectrum c) and the catalyst turned white. When the catalyst was treated at 550 °C (spectrum d), the original adsorption feature was almost completely restored.

These spectral data indicate that in the presence of H<sub>2</sub>O<sub>2</sub> or TBHP titanium hydroperoxo catalytic species are formed (by cleavage

of Ti–O–Si and Ti–OH bonds) in NH TiO<sub>2</sub>-SiO<sub>2</sub>. After the thermal treatment the peroxo groups are removed and the Ti sites appear entirely restored. There is no formation of extraframework TiO<sub>2</sub>, which means that the cleavage of Ti–O–Si bonds is largely reversible. This behavior probably results from the high crosslinking degree of non-hydrolytic xerogels.

## 4. Conclusion

Titanosilicates are among the most attractive solid oxidation catalysts for academic and commercial applications. However, in this family, only few materials with porosity in the range of the mesopores showed real catalytic potential for oxidation reactions with H<sub>2</sub>O<sub>2</sub>. In this study, we investigated the catalytic activity and selectivity of a mesoporous TiO<sub>2</sub>-SiO<sub>2</sub> xerogel in the oxidation with H<sub>2</sub>O<sub>2</sub> of a wide range of model bulky organic compounds, from styrene to 4,6-dimethyl-dibenzothiophene. High conversions and selectivities were obtained under mild conditions for most substrates. In addition, the H<sub>2</sub>O<sub>2</sub> efficiency was excellent (70–95%). The catalytic performances of this amorphous TiO<sub>2</sub>-SiO<sub>2</sub> xerogel could be related to its exceptional mesoporous texture and also to the very high degree of condensation typical of non-hydrolytic xerogels that probably accounts for both the low hydrophilicity of the surface and the stability of the Ti sites after exposure to aqueous H<sub>2</sub>O<sub>2</sub>. It has been shown that this large-pore TiO<sub>2</sub>-SiO<sub>2</sub> xerogel is active for the selective oxidation of thiophene derivatives to the corresponding sulfones, whereas the medium-pore zeolite TS-1 is totally inactive in the oxidation of polyaromatic sulfur compounds with H<sub>2</sub>O<sub>2</sub>. Accordingly, such mesoporous NH TiO<sub>2</sub>-SiO<sub>2</sub> xerogels are promising catalysts for the mild synthesis of fine chemicals and for environmental applications.

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